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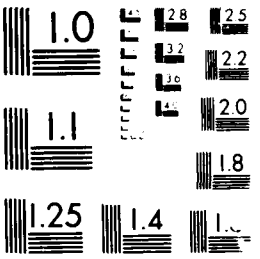

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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

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Ecole Polytechnique Fédérale de Lausanne

DAJA45-85-C-0026, P00001

Fifth Interim Report
January - September 1987

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SUMMARY

In the second year of contract, the following parts of the original project have been accomplished:

1. Model calculations of the kinetics of the decomposition of H_2O_2 in H_2O and fitting of the model of sequence and rates of reactions to the experimental results.

2. Synthesis of perfluoro 2-methyl-2-propanol

3. Formulation of microemulsions containing totally perfluorinated components:
- sodium perfluorocaprylate
- perfluoro n-hexane
- perfluoro 2-methyl-2-pentanol or perfluoro t-butanol
- water

SHORT TERM PROJECTS

The projects for the third year of contract have already been transmitted (1). The work will be done in close collaboration with Dres. M.-T. Maurette and E. Oliveros (Université Paul Sabatier, Toulouse).

MECHANISM OF H_2O_2 DECOMPOSITION. MODEL CALCULATIONS AND KINETIC EXPERIMENTS

After having accomplished an extensive investigation on the kinetics of H_2O_2 decomposition in H_2O and in perhydrogenated four components microemuélsions (s.Final Report, 1986) we began in this second year of contract to study some sequences of reactions which may be of importance for the observed decomposition oh H_2O_2 and which could be fitted to the experimental kinetic results in using rate constants independently determined.

The general scheme of reactions comprises:

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \quad (1)$$

$$H_2O_2 + HO_2^- \rightleftharpoons OH\cdot + O_2^{-}\cdot + H_2O \quad (2)$$

$$O_2^{-}\cdot + H_3O^+ \rightleftharpoons HO_2\cdot + H_2O \quad (3)$$

$$O_2^{-}\cdot + HO_2\cdot \longrightarrow O_2 + HO_2^- \quad (4)$$

$$O_2^{-}\cdot + O_2^{-}\cdot + H_2O \longrightarrow O_2 + HO_2^- + HO^- \quad (5)$$

$$O_2^{-}\cdot + HO\cdot \longrightarrow O_2 + HO^- \quad (6)$$

$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \quad (7)$$

$$HO\cdot + H_2O_2 \longrightarrow HO_2\cdot + H_2O \quad (8)$$

$$HO\cdot + HO\cdot \longrightarrow H_2O_2 \quad (9)$$

$$2\,H_2O \rightleftharpoons HO^- + H_3O^+ \quad (10)$$

The rate and equilibrium constants have ben taken as determined and published independently by different authors[3-9]:

$K_1 = 2.4 \times 10^{-12}$ M [3]

$k_2 = 8.6 \times 10^{-6}$ M^{-1}s^{-1} [3]

$k_3 = 4.7 \times 10^{10}$ M^{-1}s^{-1} [4]

$K_3 = 1.49 \times 10^{-5}$ M [4]

$k_4 = 8.5 \times 10^{7}$ M^{-1}s^{-1} [5]

$k_5 = 6$ M^{-1}s^{-1} [6]

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$k_6 = 1 \times 10^{10}\ M^{-1}.s^{-1}$ 6

$k_7 = 8.5 \times 10^{5}\ M^{-1}.s^{-1}$ 7

$k_8 = 2.65 \times 10^{7}\ M^{-1}.s^{-1}$ 8

$k_9 = 5.5 \times 10^{9}\ M^{-1}.s^{-1}$ 9

$k_{10} = 1.3 \times 10^{11}\ M^{-1}.s^{-1}$ 10

$K_{10} = 10^{-14}\ M$

The fitting to our experimental results (o) is shown in figures 1 and 2. The model fits in fact excellently yielding only slight changes for k_1 and k_5, as well as a major variation on k_3 which has to be taken as a first order rate constant ($7.0 \times 10^{5}\ s^{-1}$).

A complete fitting requires some experiments with times of reaction between 700 and 1000 h in order to confirm the acceleration of the reaction, as predicted by the model (figures 1 and 2). These experiments are currently undertaken in an appropriately stabilized equipment. The results already obtained confirm qualitatively the shape of the calculated curves.

SYNTHESIS OF PERFLUORINATED 2-METHYL-2-PENTANOL

Perfluoro 2-methyl-2-pentanol has been prepared using and optimizing the procedure of K.V. Scherer, Jr. et al.[11]:

$$CF_3\text{-}CF_2\text{-}CF{=}C(CF_3)_2 \xrightarrow{KF,\ N_2O_4,\ DMA} CF_3\text{-}CF_2\text{-}CF_2\text{-}C(CF_3)_2NO \qquad (11)$$

$$CF_3\text{-}CF_2\text{-}CF_2\text{-}C(CF_3)_2NO \xrightarrow{O_2}$$

$$\longrightarrow CF_3\text{-}CF_2\text{-}CF_2\text{-}C(CF_3)_2ONO \qquad (12)$$

$$CF_3\text{-}CF_2\text{-}CF_2\text{-}C(CF_3)_2ONO \xrightarrow{H_2O}$$

$$\longrightarrow CF_3\text{-}CF_2\text{-}CF_2\text{-}C(CF_3)_2OH \qquad (13)$$

The synthesis is currently untertaken on a level of 50 g of substrate in order to prepare sufficient material for the planned kinetic experiments.

FORMULATION OF NEW MICROEMULSIONS CONTAINING THREE PERFLUORINATED COMPONENTS AND WATER

Following the procedure already published[12], three new pseudo-ternary phase diagrams have been established concerning the following formulations:

- sodium perfluorocaprylate/perfluoro 2-methyl-2-pentanol (1/1), perfluoro n-hexane, water (figure 3)

- sodium perfluorocaprylate/perfluoro 2-methyl-2-pentanol (1/2), perfluoro n-hexane, water (figure 4)

- sodium perfluorocaprylate/perfluoro t-butanol (1/2), perfluoro n-hexane, water (figure 5)

CONCLUSION

The results of the work made possible through this contract provide the basis for
- the confirmation of the observed carboxylate catalyzed decomposition of H2O2 in perfluorinated microemulsions,
- the determination of OH. radical recombination in a chemically inert environment,

- the application of perfluorinated microheterogeneous media for oxidation reactions and efficiency determinations with respect to aqueous and perhydrogenated microheterogeneous media.

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FINANCIAL STATEMENT

As of August 30, 1987, SFR 57534.30 have been paid in selaries and chemicals leaving an uncovered balance of SFR 34766.50 since the last payment due June 30, 1987 has not yet been credited.

Lausanne, October 24, 1987

André M. Braun

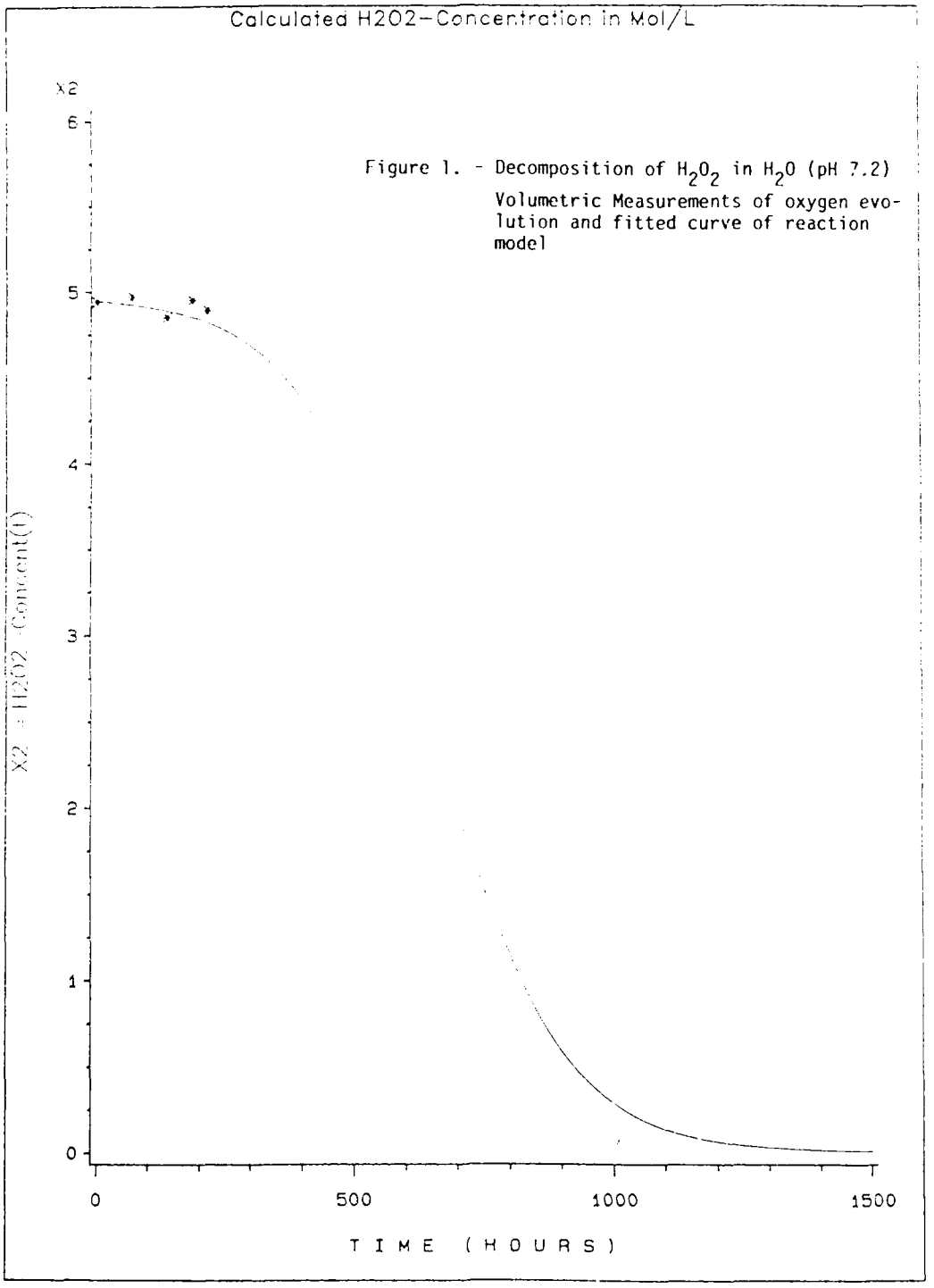


Figure 1. - Decomposition of H_2O_2 in H_2O (pH 7.2)
Volumetric Measurements of oxygen evolution and fitted curve of reaction model

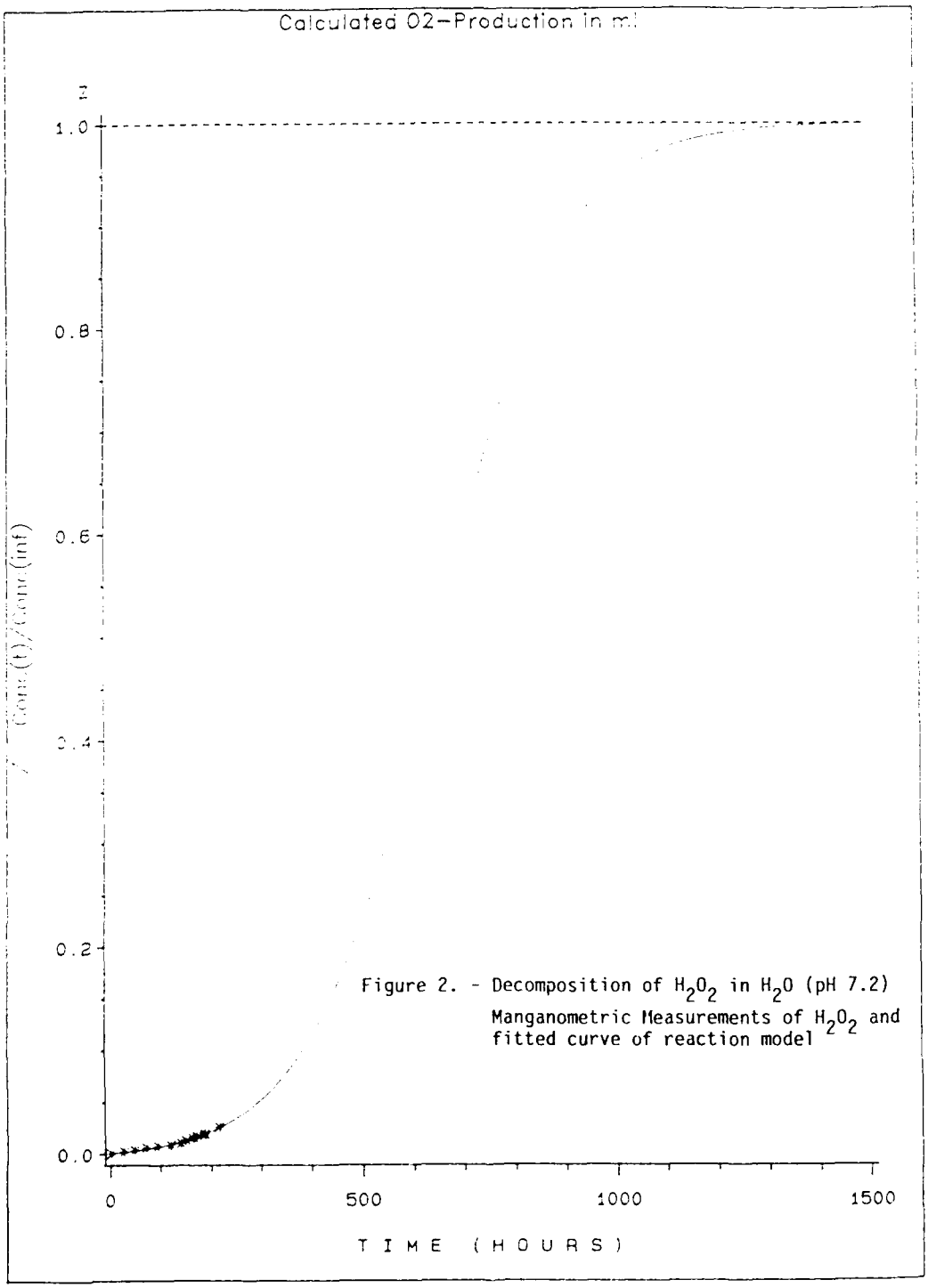


Figure 2. - Decomposition of H_2O_2 in H_2O (pH 7.2)
Manganometric Measurements of H_2O_2 and fitted curve of reaction model

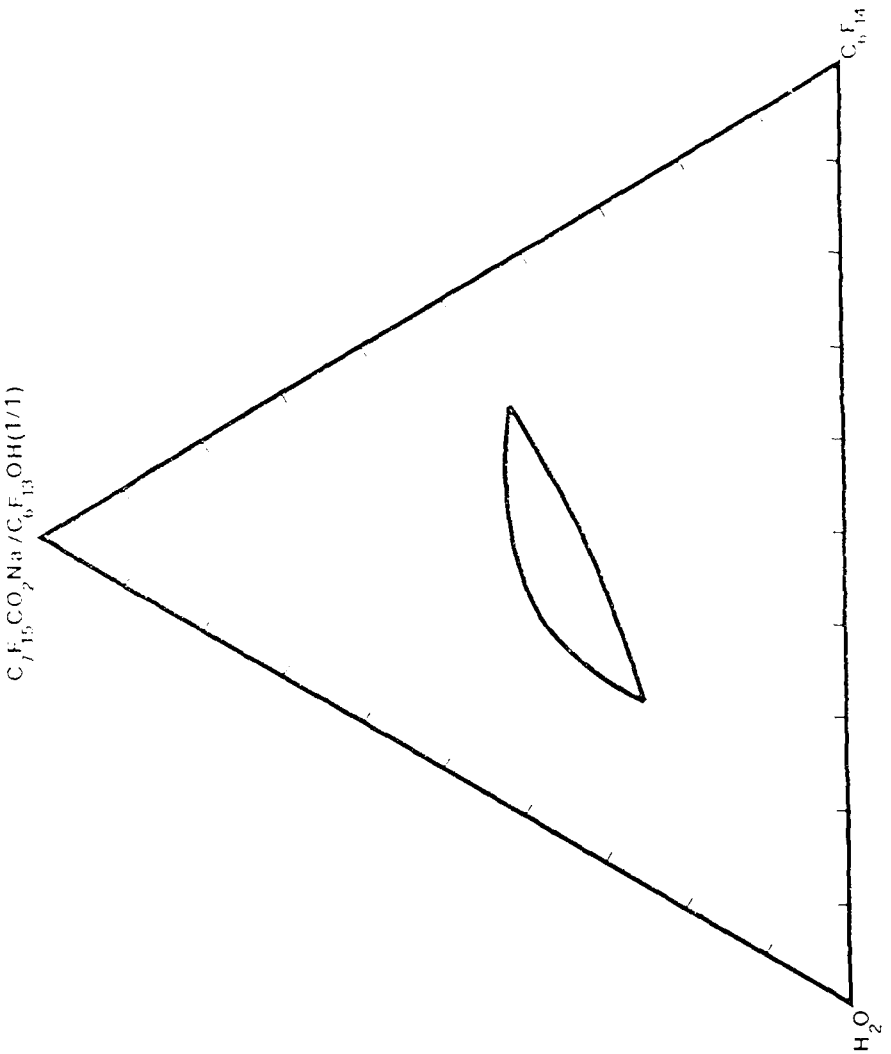


Figure 3. - Pseudo ternary phase diagram of a mixture of sodium perfluoro-caprylate/perfluoro 2-methyl-2-pentanol (1/1), perfluoro n-hexane and water

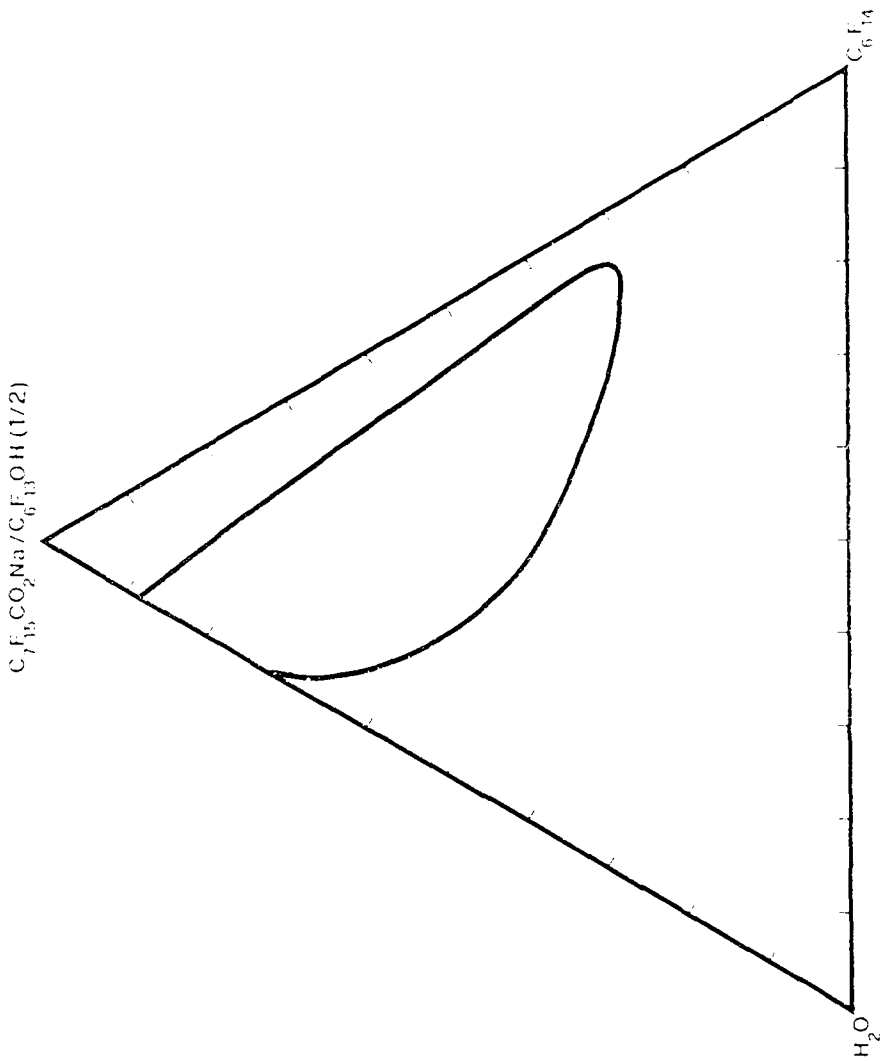


Figure 4. - Pseudo ternary phase diagram of a mixture of sodium perfluoro-caprylate/perfluoro 2-methyl-2-pentanol (1/2), perfluoro n-hexane and water

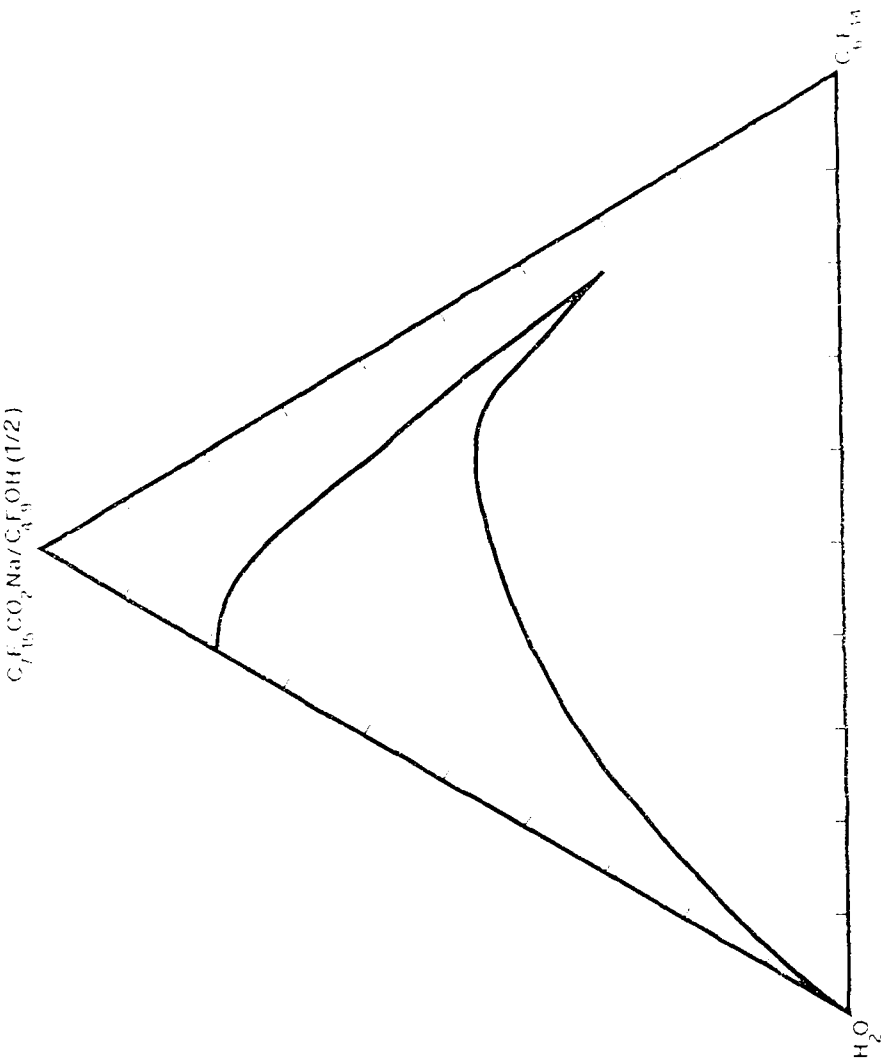
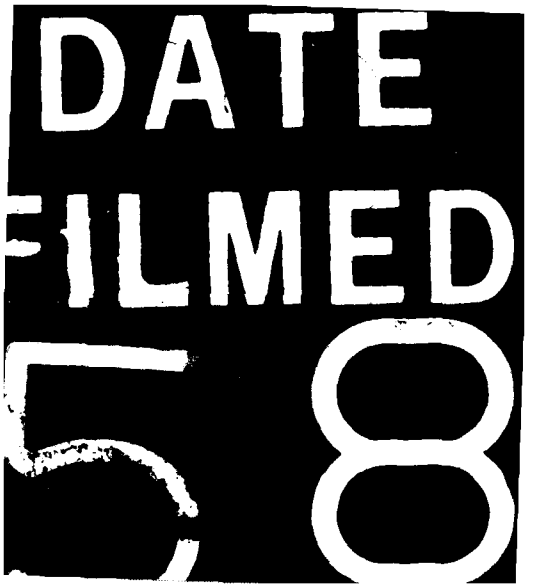


Figure 5. - Pseudo ternary phase diagram of a mixture of sodium perfluorocaprylate/perfluoro t-butanol (1/2), perfluoro n-hexane and water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